



# Rational design of photo–/electro–catalytic systems for the transformation of plastic wastes

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## ABSTRACT

The indiscriminate disposal and inadequate treatment of plastic wastes have caused severe global environmental and ecological crisis. Economically viable and energy-efficient technologies should be explored for the transformation of plastic wastes. Photo–/electro–catalytic technologies driven by the renewable energy under mild conditions have been widely developed to transform plastic wastes into valued chemicals and fuels. This review summarizes the recent progress on design strategies of catalytic systems for the selective cleavage of chemical bonds in plastic polymer chains. The correlation between catalyst features and catalytic performance in the plastic transformation have been systematically discussed in each section. This review highlights the advantages of plastic waste transformation via sustainable photo–/electro–catalytic technologies to create a circular economy with low carbon emissions.

## 1. Introduction

With the rapid global industrialization and improvement of living standards of human beings, plastic products have been widely utilized in various industrial and daily lives because of their convenience, durability, versatility, processability and cost-effectiveness [1]. Over the past few decades, the annual production of plastics has increased to hundreds of millions of tons. During the COVID–19 pandemic, the manufacture and usage of single-use plastics have rapidly increased, especially in the medical, packaging, and catering industries [2,3]. Although the high chemical stability of plastics is advantageous for usage, their slow decomposition kinetics in the eco-system trigger a series of environmental crises [4]. A large amount of disposable plastic released into aquatic and terrestrial eco-systems will be degraded into micro-sized fragments, which can eventually enter the food web and adversely affect public health [4,5]. Researchers predicted that the life cycle of global plastic products will contribute approximately 6.5 Gt of CO<sub>2</sub>–equivalent greenhouse gas (GHG) emissions by 2050, responsible for a large portion of the global carbon budget [6]. Therefore, effective technologies for the treatment of plastic wastes should be developed to alleviate the negative impacts on the natural environment.

To address these issues, a series of treating methods against the plastic wastes have been developed. Among them, landfills and incineration are most commonly adopted [7]. For the economical and convenient purposes, a large amount of plastic wastes were treated by landfills in the past [8]. However, landfills can result in the severe waste of land resources, soil poisoning, and loss in crop productivity. Compared with landfills, the incineration method can utilize the high energy value of polymers [9]. Nonetheless, GHG emissions and the generation of harmful substances during incineration could also cause environmental issues [10]. Besides, mechanical reprocessing is widely used to recover plastic wastes to manufacture products with properties similar to those of the original plastics [11]. However, various performance parameters of the reprocessed plastic products are always substantially decreased and inferior to those of original plastic products after harsh reprocessing processes [12]. Generally, mechanical reprocessing is always regarded as down-cycling process. Thus, research should focus on the development of efficient and sustainable technologies to recover the chemical value and alleviate the environmental pollution of plastic wastes [13].

Notably, chemical recycling strategies exhibit immense potential for the transformation of plastic wastes, which provide a

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“waste-to-wealth” route to produce value-added products and industrial feedstocks [14,15]. In 2019, the International Union of Pure and Applied Chemistry (IUPAC) has identified polymer-waste recycling as one of the top-10 emerging technologies in chemistry, which contributes to the alleviation of environmental pollution and energy crisis by constructing a circular economy [16]. Compared with landfills, incineration and mechanical methods, appropriate chemical strategies can transform plastic wastes into products with similar or higher utility and value than the original plastic products, which is promising for the treatment of plastic wastes [17].

Among the chemical recycling strategies, catalytic recycling technologies have emerged as methods that can increase the overall benefits and sustainability of plastic conversion, regarded as promising routes to resolve the pollution problems [18–20]. These catalytic technologies can selectively break the chemical bonds and utilize the potential value of carbon, hydrogen, and oxygen elements in polymer chains to obtain valued chemicals and fuels [21,22]. Besides, catalytic recycling strategies can significantly reduce energy consumption and ameliorate the reaction conditions by the rational design of catalysts and catalytic systems [23]. At present, catalytic conversion technologies mainly include thermocatalysis [24], photocatalysis [25], electrocatalysis [26], and enzymatic catalysis [27]. Among these catalytic strategies, photo- and electro-catalysis, which can be driven by renewable energy at ambient temperature and pressure, provides an appealing approach for the transformation of plastic wastes to produce a variety of useful chemicals.

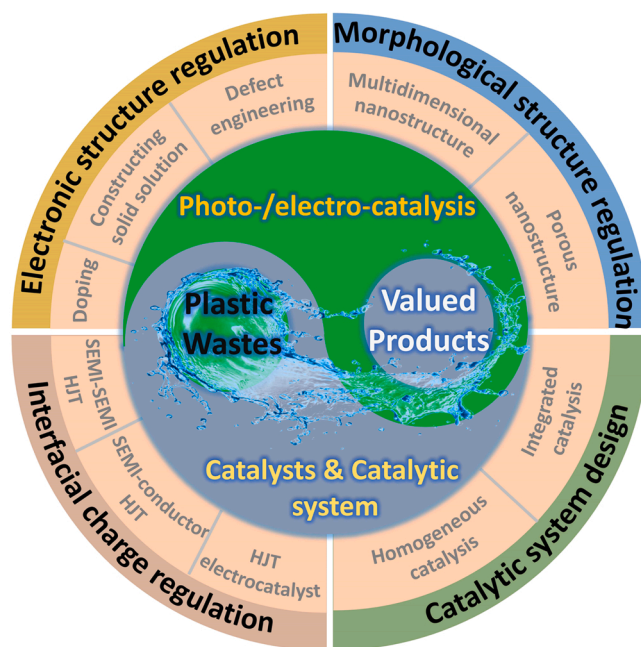
With the renewable and sustainable solar irradiation as the direct energy input, photocatalysis strategy, which is widely investigated to mimic the photosynthetic process in plants and produce solar fuels and products, is generally recognized as a cost-effective, energy efficient and environmentally friendly way to valorize plastic wastes [28,29]. In 1981, Sakata et al. reported that the  $\text{TiO}_2$  photocatalyst can transform polyvinyl chloride polymers into  $\text{CO}_2$  accompanied with hydrogen generation, showing the potential of photocatalysis technology for the reforming of plastic wastes [30]. Since then, researchers have widely investigated the photocatalysis technology for photodegrading plastic wastes into  $\text{CO}_2$  or photo-reforming plastic wastes into hydrogen or other valued chemicals [31–33]. During the photocatalytic process, a few key technical aspects should be considered. First, screening and utilizing of photocatalysts with energy band structures that are well matched with the redox potentials of targeted reactions. Second, improving the absorption ability of solar energy (especially the visible light region) of photocatalysts by doping or modification of the catalysts. Third, facilitating the separation and transportation of photogenerated carriers by introducing an electron and/or hole transport layer. Finally, providing sufficient active sites for the substrates (by cocatalyst loading) to improve the extraction and consumption rates of the photogenerated carriers. Due to the tunable physical and chemical properties of photocatalysts for the reactivity manipulation, various strategies have been reported to enhance the photocatalytic performance for the conversion of plastic wastes [34–36].

Compared with photocatalysis directly driven by solar energy, electrocatalysis, which can be driven by renewable electricity derived from solar or wind energy, is also regarded as an efficient, low-cost and scalable technology for the energy conversion [37], chemical synthesis [38], and waste recycling [39]. Recently, some reports on electrocatalytic conversion of plastic wastes have emerged and showed great potential for the valorization of plastic wastes [26,40]. Compared with other technologies, there are some advantages of the electrocatalysis technology for the conversion of plastic wastes to produce value-added chemicals. First, plastic wastes can be efficiently upcycled to valuable chemicals and industrial feedstock at mild conditions with high efficiency and selectivity [26]. Second, during the electro-reforming of plastic wastes, the electrons and protons released from the anode can be collected by the cathode to generate hydrogen or liquid fuels, which exhibits immense potential for sustainable energy production [37].

Third, the electro-reforming strategy transforms the discontinuous and variable renewable electrical energy into chemical energy that can be easily stored and transported [41]. Fourth, the selectivity of the conversion reactions can be regulated by the rational design of electrocatalysts or reactor configuration [42]. Therefore, the electrocatalytic strategy also provides an efficient route for the transformation of plastics to alleviate the pollution problems and increase the waste values.

For the catalytic transformation of plastic wastes driven by renewable energy, the interfaces between catalysts and plastic wastes should be delicately designed to improve the catalytic conversion efficiencies [43,44]. Since plastic wastes generally exist as solid-state at the normal temperature and pressure, the poor water solubility of the plastic wastes will greatly limit the reactivities due to the existence of solid-solid reaction interface to retard the reaction. Given this problem, two main strategies can be employed to manipulate the reaction interface. One is adopting the pretreatment process to transform plastic wastes into water-soluble organic small molecules, which can realize liquid-solid heterogeneous catalytic system [26,40]; and the other is replacing aqueous system with organic system to dissolve plastic wastes in the organic solvent, which can achieve homogeneous catalysis or liquid-solid heterogeneous catalysis according to the solubility of the catalysts [45]. For the polyester plastic wastes, there are abundant ester and amido bonds in the polymer chains, which can be easily depolymerized by the solvolysis treatment to generate monomer compounds. In contrast, for the polyolefin plastic wastes, the molecular structure of the polymer is generally constituted with inert C–C and C–H bonds, which require highly active free radical species to activate and transform these plastics.

A series of reviews and perspectives have been reported for the catalytic transformation of plastic waste from different perspectives, such as plastic types, converted products or conversion technologies and so on [20,21,46,47]. In this review, we aim to summarize the photo-/electro-catalysis investigation progress and key design principles of the catalysts or catalytic systems to selectively break the chemical bonds for the efficient transformation of plastic wastes, as shown in Fig. 1. The regulation strategy of catalysts and structure-function relationship between catalysts (component, structure, interface) and performance (e.g., activity, selectivity and bond cleavage) have been systematically



**Fig. 1.** Regulation strategies of catalysts and catalytic systems for plastic wastes conversion into valued products by photo-/electro-catalysis technology under mild conditions.

summarized and evaluated. Finally, the importance and future prospect of interdisciplinary research activities and the integration of various catalytic technologies with renewable energy input have been discussed. We hope this review will help researchers to improve their understanding of photo-/electro-catalytic technologies and provide insight for the development of plastic wastes treatment in the future. We believe that the sustainable catalytic technologies for the transformation of plastic waste could mitigate the global issue of plastic pollution and promote the development of circular economy.

## 2. Electronic structure regulation

The catalytic activities of photocatalysts or electrocatalysts are closely related to their electronic structures. The electronic band structure of a photocatalyst plays an essential role in its light absorption capacity (especially for the visible-light region), and the concentration and mobility of photogenerated charge carriers as well as their redox capacities [48]. Likewise, the electronic structure of an electrocatalyst strongly influences its thermal and electrical conductivity, the adsorption/desorption behaviors of key intermediates, and the reaction energy barrier of the rate-limiting step [49]. At present, the electronic structure regulating strategies are widely used in the field of photo-/electro-catalytic transformation of plastic wastes, including the introduction of external impurities as a doping strategy, the fabrication of multi-component solid solution as an alloying strategy, and the introduction of structural defects, namely defect engineering strategy, as shown in Fig. 2.

### 2.1. Doping

In the photo-/electro-catalytic systems, doping is regarded as an appealing way to effectively regulate the electronic structures of photocatalysts and electrocatalysts. The introduction of external impurity into the semiconductor as a dopant can (1) create electronic states, including the donor levels above the valence band and/or the acceptor levels below the conduction band, (2) tune the energy band structure, especially the positions of the conduction band minimum (CBM) and the valence band maximum (VBM), (3) promote the absorption and utilization of visible light region, (4) accelerate the transfer kinetics of photogenerated electrons and holes, and (5) govern the exposed crystal facet or even the crystal phase [50]. By contrast, the introduction of foreign atoms into the electrocatalyst can (1) modulate the local charge distribution, (2) increase the electrical conductivity and electron density, (3) provide active sites for the reactive substrates and (4) govern the adsorption and activation behaviors of critical intermediates to reduce

the reaction energy barriers [51]. Given the above advantages, doping strategy has been widely adopted in the field of photo-/electro-catalytic transformation of plastic wastes into valued chemicals and/or high-energy hydrogen fuels.

In terms of photocatalytic transformation of plastic wastes, visible-active N-doped TiO<sub>2</sub> photocatalyst was first applied to the conversion of plastic wastes to inorganic small molecules (CO<sub>2</sub>, H<sub>2</sub>O) in the early studies [52,53]. Although the direct mineralization and degradation can alleviate the current plastic problem to some extent, the selective transformation of plastic wastes into value-added chemicals can better extract the economic value and energy storage within the discarded plastics. An illuminating pathway is to oxidize polymers to CO<sub>2</sub> by utilizing the photogenerated holes or derived reactive oxygen species, while reducing CO<sub>2</sub> to obtain carbonaceous chemicals and fuels in the presence of water by utilizing the concurrent photogenerated electrons. To this end, it is necessary to elaborately design photocatalysts with energy band structures that cover the redox potentials of the above reactions. Considering the above guidelines, the Ga<sub>2</sub>O<sub>3</sub> semiconductor material, with a VBM at ca. + 3.16 V vs. RHE and a CBM at ca. - 1.62 V vs. RHE, can be considered as ideal candidates. However, its wide band gap seriously limits its visible-light harvesting capacity, which can be effectively solved by the doping strategy. Xie et al. designed a Co-doped Ga<sub>2</sub>O<sub>3</sub> photocatalyst for the plastic-to-syngas conversion [54]. The introduction of Co component effectively regulated the band structure of Ga<sub>2</sub>O<sub>3</sub> semiconductor through d-d internal transitions, and thus promoted the visible-light absorption. In addition, Co dopant distinctly enhanced the density of states (DOS) at the valence band edge, contributing to the fast migration of photogenerated charge carriers, as shown in Fig. 3A. Moreover, it was revealed that the doped Co also resulted in the charge accumulation on Co and adjacent Ga as well as on Co-H bonds, which contributed to the stabilization of \*COOH intermediate on Co-Ga double active site and \*H intermediate on Co active site. The consequent decreased formation energies of \*COOH and \*H intermediate were beneficial to the selective reduction of CO<sub>2</sub> to CO and H<sub>2</sub>O to H<sub>2</sub> [54].

Compared with metal oxide photocatalysts, non-metal-based graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) photocatalysts suffer from problems such as limited light absorption capacity and high photogenerated carrier recombination rate. To overcome this limitation, Huang et al. synthesized a benzenesulfonyl chloride incorporated g-C<sub>3</sub>N<sub>4</sub> (BS-CN) photocatalyst for photo-reforming polylactic acid (PLA) [55]. The introduction of aromatic benzene ring in g-C<sub>3</sub>N<sub>4</sub> structure can not only enhance the delocalization of  $\pi$  electron to narrow the bandgap of the g-C<sub>3</sub>N<sub>4</sub> photocatalyst, but also establish intramolecular charge transfer (ICT) from the HOMO of g-C<sub>3</sub>N<sub>4</sub> to the LUMO of electron-withdrawing aromatic to inhibit the non-radiative recombination of photogenerated charge carriers. By loading hydrogen evolution cocatalyst, the Pt-loaded (1 wt%) BS<sub>5</sub>-CN photocatalyst achieved a high hydrogen production rate, and simultaneously converted lactic acid molecules derived from PLA hydrolysate into valued formic acid and acetic acid under the visible light irradiation [55].

In terms of electrocatalytic transformation of plastic wastes, doping strategy provides a promising prospect for the electrocatalytic oxidation of ethylene glycol (EG) molecules derived from the PET hydrolysate into high-value products, whose selectivity can be precisely modulated via the heteroatom dopants. For example, Zhao et al. constructed an electrocatalytic coupling system, including an anodic NiCo<sub>2</sub>O<sub>4</sub>-catalyzed PET reforming process and a cathodic SnO<sub>2</sub>-catalyzed CO<sub>2</sub> reduction process, to coproduce the formic acid (FA) as a perfect hydrogen storage carrier [40]. The Ni-Co dual active sites favor the selective oxidation of EG to FA via a possible reaction pathway involving \*OCH<sub>2</sub>-H<sub>2</sub>CO\* and \*OCH-HCO\* intermediates. Lately, Chen et al. also reported a CuCo<sub>2</sub>O<sub>4</sub>-based electro-reforming process of polyester plastics [56]. By comparison with Co<sub>3</sub>O<sub>4</sub> and CuO electrocatalysts, the synergistic effect of Cu and Co atoms was demonstrated to regulate the adsorption and activation behaviors of EG\* and OH\* intermediates with more existing empty

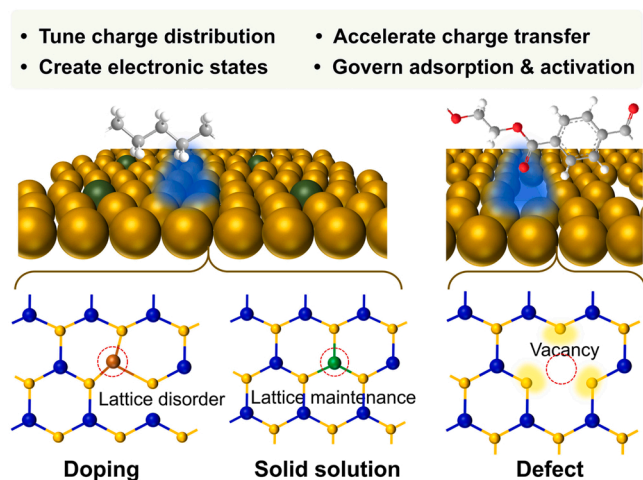
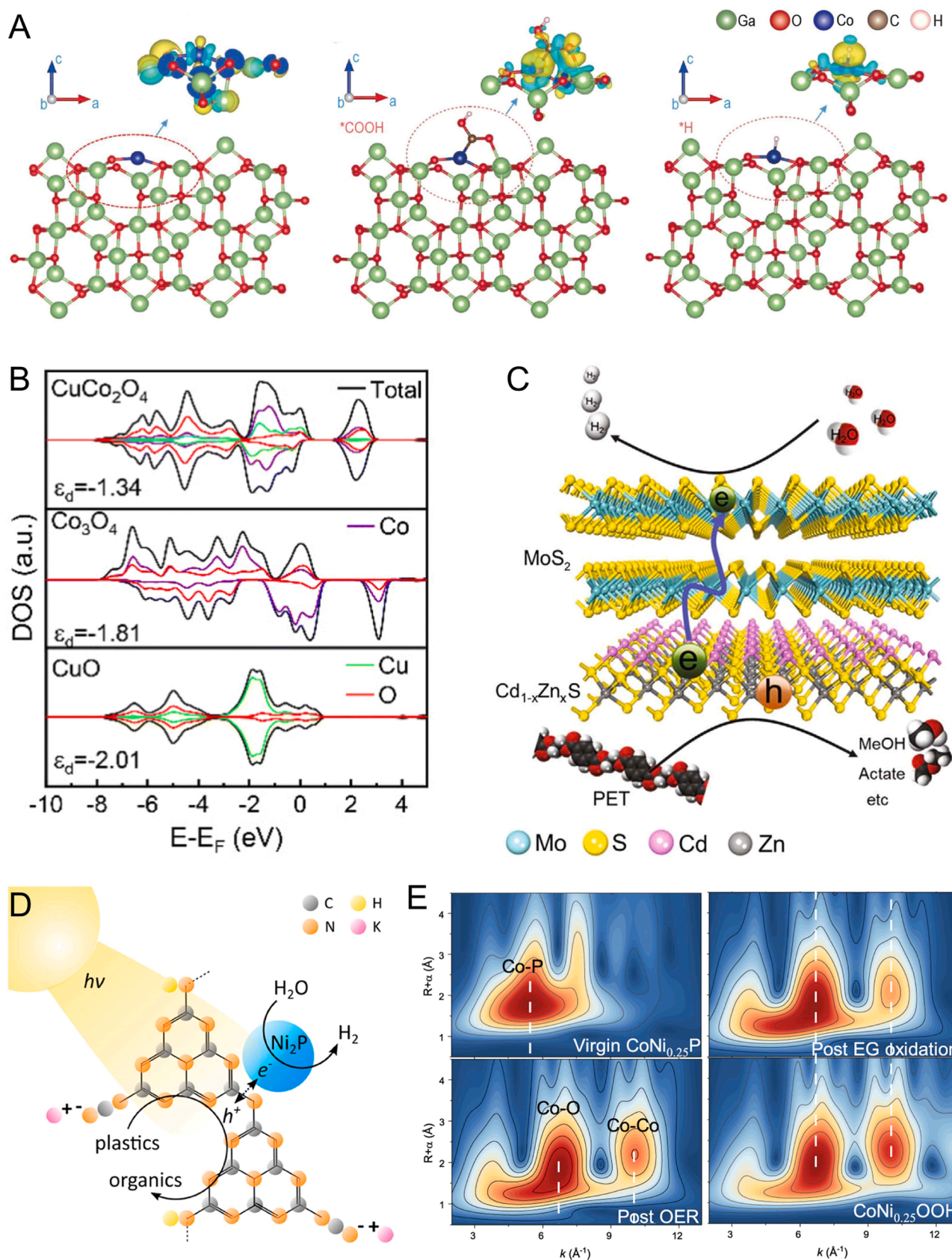


Fig. 2. Schematic illustration of electronic structure regulation strategy for the photo-/electro-catalytic transformation of plastic wastes.





**Fig. 3.** (A) The charge density maps of the Co-Ga<sub>2</sub>O<sub>3</sub> photocatalyst under the different adsorbed states [54]. Copyright 2022, Oxford University Press. (B) Calculated density of state of CuCo<sub>2</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, and CuO electrocatalysts [56]. Copyright 2022, Royal Society of Chemistry. (C) The mechanism of H<sub>2</sub> evolution coupled with the conversion of PET plastic over MoS<sub>2</sub>/Cd<sub>1-x</sub>Zn<sub>x</sub>S [57]. Copyright 2020, Wiley-VCH GmbH. (D) Schematic diagram of the plastics photo-reforming coupled process using a CN<sub>x</sub>|Ni<sub>2</sub>P photocatalyst [31]. Copyright 2019, American Chemical Society. (E) Wavelet transforms for Co K-edge EXAFS spectra of CoNi<sub>0.25</sub>P before and after electrolysis [26]. Copyright 2021, Springer Nature.



antibonding states, as shown in Fig. 3B.

The above studies verified the feasibility of the doping strategy in the photo- /electro-catalytic transformation of plastic wastes. The synergistic effect of foreign atoms to tune the electronic structure and modulate the surface behaviors of key intermediates deserves more in-depth investigation. In addition, it is worth noting that the doping content also has a close relationship with the catalytic activity. The excess heteroatoms may induce the undesirable effects, such as the possible formation of recombination sites in the photocatalysts or secondary phases in the electrocatalysts. Therefore, the dopant category and concentration are two key factors in the future development of photo- /electro-catalytic transformation of plastic wastes.

## 2.2. Constructing solid solution

The multi-component solid solution is a single-phase substance in which the solute atoms are dissolved in the solvent lattice while still maintaining the crystallographic form of the solvent [58]. The multi-component solid solution is commonly found in alloys and transition metal compounds (TM-Xides, X = C, N, P, S), mainly divided into substitutional and interstitial solid solution [59]. Constructing solid solution usually involves two or more semiconductors or electrocatalysts with the same physicochemical characteristics but different photo- /electro-catalytic performances. In the former case, the formation of photocatalyst solid solution can make a precise design of the bandgap and band edge positions, and a concentration gradient will also bring a gradient energy band conducive to the cascade charge transfer [58,60]. In the latter case, the formation of electrocatalyst solid solution can effectively regulate the charge distribution around the active sites to affect the adsorption/desorption behaviors of key intermediates [61, 62]. The strategy of constructing solid solution is also an appealing route for the photo- /electro-catalytic conversion of plastic wastes.

$\text{Zn}_x\text{Cd}_{1-x}\text{S}$ , as a representative solid solution photocatalyst, has been widely used in the photocatalytic transformation of plastic wastes [58, 63]. Compared to ZnS with a wide bandgap of 3.5 eV for the main adsorption of ultraviolet light, CdS shows a good absorption capacity for the visible-light region due to a suitable bandgap of 2.4 eV. However, due to the relatively lower CBM and higher VBM positions of the CdS semiconductor, both the reducing capacity of photoelectrons for the proton reduction and the oxidizing capacity of photoholes for the water oxidation are not satisfactory. The formation of  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  solid solution can obtain the appropriate energy band structure for the visible-light absorption capacity and the satisfactory redox capacity by precisely adjusting the Cd/Zn ratio, which is beneficial to the selective transformation of plastic wastes into target products in the photocatalytic process [63]. Zhang et al. and Zhong et al. respectively prepared a series of  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ -based photocatalyst materials with various Cd/Zn ratios, and successfully employed them for the hydrolysis-assisted photo-reforming process of PET plastic wastes [57,64]. With the modification of cocatalysts ( $\text{MoS}_2$  and MXene) for the hydrogen generation, the transfer kinetics of photogenerated charge carriers was effectively improved, as shown in Fig. 3C. The photogenerated electrons transfer to the active sites of cocatalysts and reduce protons to produce hydrogen, the photogenerated holes migrate to the photocatalyst surfaces to oxidize the PET hydrolysate, EG molecules to generate acetic acid, ethanol and other valued products.

As for the solid solution utilized in the electrocatalytic transformation of plastic wastes, both noble-metal alloys and multi-component transition-metal phosphides have been exploited as the cost-effective and scalable solid solution electrocatalysts. Pd was demonstrated as a feasible electrocatalyst for the PET electro-reforming to obtain the fuel-cell-grade hydrogen on the cathode as well as terephthalates and carbonates on the anode [65]. The proposed working mechanism revealed that the Pd-catalyzed C-C bond cleavage of the  $\text{HOOC-COOH}$  intermediate resulted in the formation of carbonates with a high selectivity. However, the scarce reserves and high expenses of

noble metal Pd severely restrict the future up-scaling applications, which can be resolved by alloying Pd with various earth-abundant and cost-effective transition metals. For example, Reisner et al. developed a  $\text{Cu}_{30}\text{Pd}_{70}$  alloy electrocatalyst for the reforming of PET plastic into the valued glycolic acid driven by a perovskite-based photocathode [29]. The introduction of Cu species caused a down-shift in the d-band center of Pd, which favored the adsorption/desorption dynamics of  $\text{OH}_{\text{ads}}$  and EG molecules, lowering the onset potential and increasing the Pd poisoning tolerance. In addition to the regulating functions of the alloying strategy on the electrocatalytic activity and product selectivity, the researchers also highlighted the significance of the spatially separated redox reactions and the substitution of semiconductor suspension system in the unassisted PEC systems [29].

Advantages of the constructing solid solution strategy have been demonstrated for the effective and selective photo- /electro-catalytic transformation of plastic wastes. The synergistic effects of solute and the solvent atoms on the electronic structures contribute to increasing active sites and active species for the reactant conversion. Likewise, the ratio of solute and the solvent atoms or the alloying degree has a profound effect on the catalytic activity and the selectivity towards target products. The optimization of components in the solid solution to leverage the economic and performance aspects deserves more attention for the future photo- /electro-catalytic transformation of plastic wastes.

## 2.3. Defect engineering

Crystal defects refer to the atomic imperfect arrangement in crystal materials. The point, line, planar, and volume defects can be determined from the missing or irregularly arranged atoms, screw or edge dislocation, grain or twin boundaries, and voids or lattice disorder, respectively [66]. In the photocatalytic technology, the spontaneous formation or intentional introduction of defects can endow semiconductor materials with better photophysical properties. The presence of defects can induce the formation of additional electronic states within the semiconductor energy band, thus significantly narrowing the bandgap of ultraviolet-active semiconductors for better visible-light absorption [66]. Moreover, regardless of photocatalytic or electrocatalytic process, the concomitant thermodynamically unstable coordinatively unsaturated atoms as well as surface dangling bonds can induce the localized charge accumulation, so that the local electronegativity and coordination environment around the active sites are precisely tuned to alter the adsorption and activation behaviors of reactive substrates on the catalyst surface [67]. Defect engineering strategy becomes another effective method for the regulation of electronic structure to achieve the efficient photo- /electro-catalytic plastic transformation process.

As mentioned above, g- $\text{C}_3\text{N}_4$  photocatalysts are widely investigated in the photocatalytic transformation of plastic wastes due to their good visible-light absorption capacity, distinctive two-dimensional microstructure, and favorable electronic structure. Even so, the sluggish transfer kinetics and the severe recombination behaviors of photo-generated charge carriers have a negative impact on the photocatalytic performances of  $\text{C}_3\text{N}_4$ -based photocatalysts, which can be well ameliorated by the rational defect engineering strategy [68]. In g- $\text{C}_3\text{N}_4$  synthesis, the precursor may undergo the incomplete condensation reaction, which will produce the intrinsic amino ( $-\text{NH}_x$ ) or cyano ( $-\text{C}\equiv\text{N}$ ) defect sites. Amino defects are regarded as a motif for the interlaminar interaction via hydrogen bonds, thus shortening the crystal plane spacing to enhance the interlayer polarization and charge transport. By contrast, the cyano defects are proved to regulate the band structure of g- $\text{C}_3\text{N}_4$  due to the high electronegativity, the introduction of defect states and the built-in electrostatic potential difference, thus contributing to the effective separation and transportation of photo-generated charge carriers [68]. Specifically, Lotsch et al. made an in-depth investigation on the photocatalytic mechanism of cyanamide moieties as surface terminations by the defect engineering [69]. On one hand, it can strengthen the interaction between g- $\text{C}_3\text{N}_4$  absorber and Pt

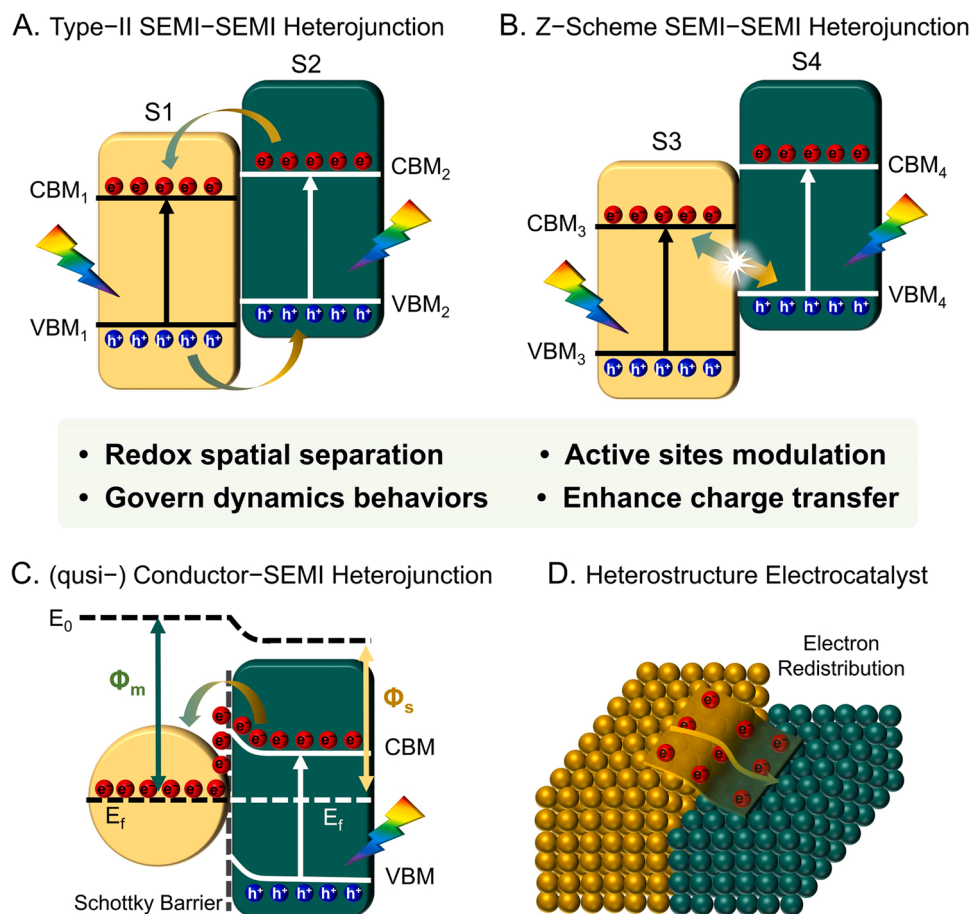
cocatalyst to promote the interfacial charge transfer. Moreover, it can induce the built-in electrostatic potential difference to enhance the effective separation of photogenerated charge carriers. Based on the above results, Reisner et al. employed the defect engineering strategy to prepare the cyanamide functionalized  $C_3N_4$ -based photocatalyst, and successfully realized the photo-reforming process of real-world polyester waste plastics under mild conditions, as shown in Fig. 3D [31]. The feasibility and techno-economic analysis were further demonstrated by the photo-reforming processes at small (2 mL) and larger (120 mL) scales and the up-scaling flow reactors containing a scalable  $25\text{ cm}^2$  photocatalyst panel [36,70].

Many previous reports have demonstrated that amorphization, defect engineering, possesses distinctive surface properties such as abundant exposed defects and dangling bonds acting as the abundant surface reactive sites. The amorphous structures can be deliberately fabricated in the synthesis process, or in-situ generated by the surface reconstruction of transition metal compounds (TM-Xides, X = C, N, P, S) [59]. A series of metal pnictides such as Co-Ni<sub>3</sub>N, CoNi<sub>0.25</sub>P and CoSe<sub>2</sub> have been employed in the electrocatalytic transformation of plastic wastes, in which a thin amorphous metal oxy/hydroxide layer can easily form on the surface of the metal pnictides [26,71,72]. The reversible redox cycles of transition metal cations in the amorphous metal oxy/hydroxide shell are proved to account for the consecutive electrocatalytic oxidation of PET-derived EG molecules, as shown in Fig. 3E. And the abundant coordinatively unsaturated atoms or dangling bonds in the amorphous metal oxy/hydroxide shell are beneficial to the charge transfer to the surface and the adsorption and activation behaviors of reactants.

Defect engineering strategy has become a satisfactory method to achieve the efficient photo-/electro-catalytic transformation of plastic wastes. The abundant coordinatively unsaturated atoms and surface dangling bonds help to modulate the adsorption and activation behaviors of reactive substrates on the catalyst surface. However, defects can also act as charge traps to lower the charge transfer efficiency. The density, location, the relative concentration ratio of bulk-to-surface defects as well as the defect stability should be placed more emphasis in the future development of photo-/electro-catalytic transformation of plastic wastes.

### 3. Interfacial charge transfer regulation

Charge transfer is the process with charge migrating from the “donor” to the “acceptor”, mainly divided into intramolecular and intermolecular charge transfer [73]. The intramolecular charge transfer is strongly correlated with the electronic structure, whose regulation has been discussed in Chapter 2. Herein, more attention is devoted to the intermolecular charge transfer between the various components in photocatalysts and electrocatalysts. Interfacial charge transfer plays a vital role on the photo-/electro-catalytic transformation of plastic wastes, providing sufficient charge carriers to reach the surface reactive sites and participate in the conversion reaction. In recent years, the research interests of interfacial charge transfer regulating strategy in the field of photo-/electro-catalytic transformation of plastic wastes, mainly focus on constructing the semiconductor-semiconductor (SEM-I-SEMI), (quasi-) conductor-semiconductor (SEMI) heterojunction photocatalysts and the hetero-structured electrocatalysts, as shown in



**Fig. 4.** Schematic illustration of interfacial charge transfer regulation strategy by constructing (A) Type-II SEMI-SEMI heterojunctions, (B) Z-Scheme SEMI-SEMI heterojunctions, (C) (quasi-) conductor-SEMI heterojunctions, and (D) heterostructure electrocatalysts for the photo-/electro-catalytic transformation of plastic wastes.

Fig. 4.

### 3.1. Constructing SEMI-SEMI heterojunction

The fast transfer kinetics of photogenerated charge carriers is a key requirement to reach a high photon-to-electron conversion efficiency in the photocatalytic process. To avoid the severe recombination phenomena in the interfaces between different components or structures, constructing semiconductor-semiconductor heterojunction is one of the most promising methods to promote the charge separation and accelerate the charge transfer kinetics driven by the built-in electric field [73, 74]. The above heterojunction refers to the constituent semiconductors in possession of the staggered band alignment, mostly involving type-II and Z-Scheme heterojunctions.

As shown in Fig. 4A, the photogenerated charge carriers form in the two semiconductors (S1 and S2) of the type-II heterojunction, the photogenerated electrons transfer from S2 to S1 driven by the built-in electric field derived from the energy level difference, while the photogenerated holes transfer in the opposite direction to realize the effective separation of photogenerated charge carriers. The accelerated charge transfer kinetics triggered by the type-II heterojunctions is conducive to promote the photocatalytic conversion efficiency of plastic wastes [75,76]. For example, Nagata et al. designed a CdS/SiC type-II heterojunction photocatalyst with the significantly enhanced charge transfer kinetics. [77] Besides, SiC moiety with defect energy levels had

strong absorption ability for visible light region on the long-wavelength side, therefore, the composite photocatalyst showed the additional thermal radiation performance. The in-situ formation of an ultrathin  $\text{CdO}_x$  layer on the CdS moiety improved the stability of the composite photocatalyst in a strongly alkaline environment. The above heterojunction photocatalyst was successfully utilized in the photo-reforming process of plastic wastes and biomass in high-temperature alkaline solution with the modification of Pt-based hydrogen production cocatalyst, as shown in Fig. 5A [77]. However, theoretical studies reveal that the actual charge transfer of type-II heterojunctions may not occur as speculated. From the thermodynamic point of view, the enhanced charge separation efficiency is at the expense of the redox capacity of the photogenerated electrons and holes. Photogenerated electrons will gather in the S1 conduction band with weak reduction ability, while photogenerated holes will gather in the S2 valence band with weak oxidation ability. Consequently, the existing electrons in the S1 conduction band will hinder electrons from S2 continuously transferring to S1 owing to the electrostatic repulsion, and so it is with photogenerated holes [73,74]. Therefore, the charge transfer mode in type-II heterojunction is still controversial.

As shown in Fig. 4B, the two semiconductors (S3 and S4) of the Z-scheme heterojunction are excited by the solar irradiation, and photogenerated electrons of S3 moiety will recombine with photogenerated holes of S4 moiety on a shuttle redox mediator or at the interface of the heterojunction in a direct Z-scheme system [78]. In

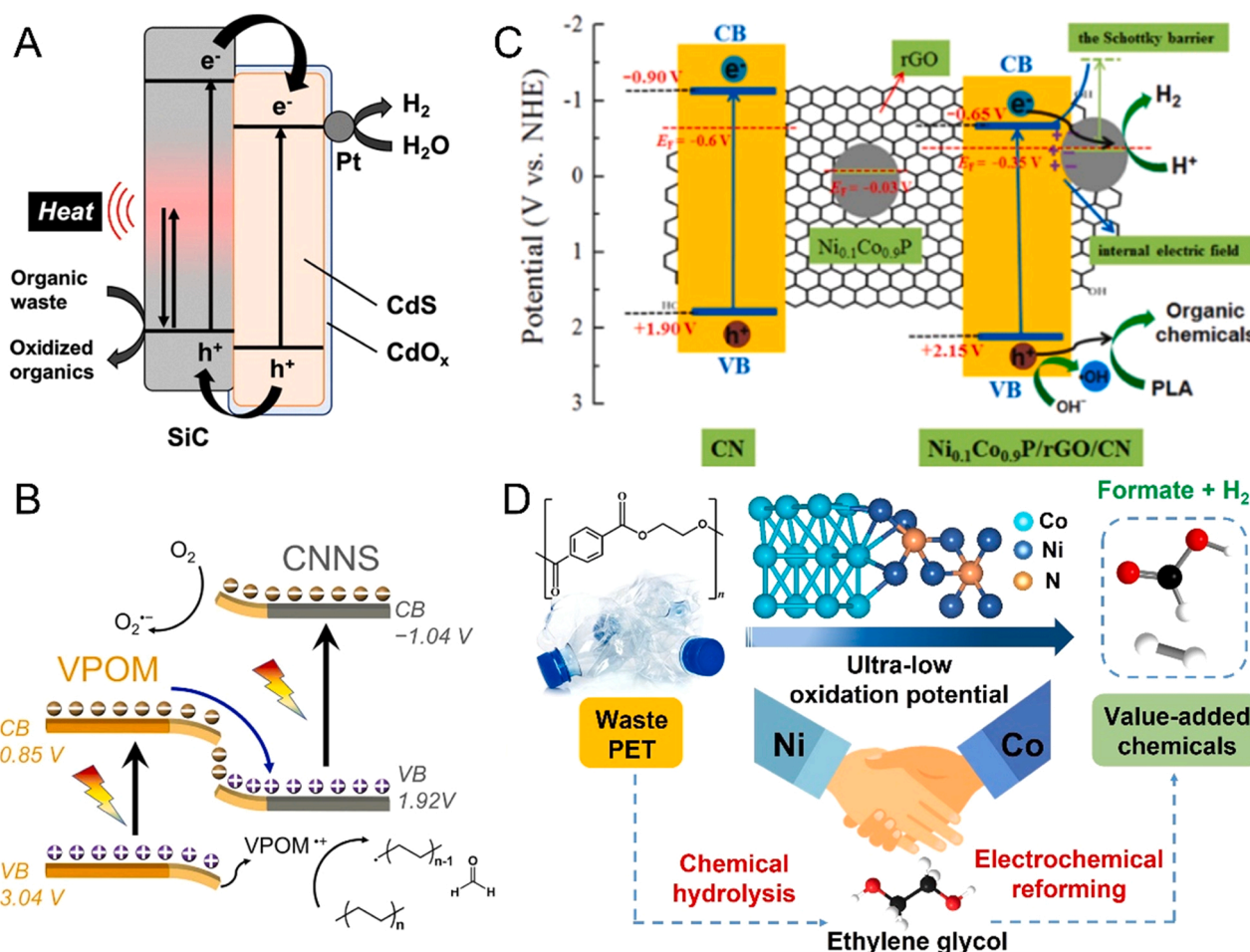


Fig. 5. (A) Schematic illustration of the photo-reforming of organic waste into  $\text{H}_2$  by Pt-deposited  $\text{CdO}_x/\text{CdS}/\text{SiC}$  heterojunction photocatalyst [77]. Copyright 2021, The American Chemical Society. (B) Schematic of the photocatalytic conversion plastic process for VPOM/CNNS Z-scheme heterojunction [79]. Copyright 2022, Elsevier. (C) The band structures of  $\text{Ni}_{0.1}\text{Co}_{0.9}\text{P}/\text{rGO}/\text{CN}$  heterojunction photocatalyst and the mechanism for photo-reforming PLA plastic [88]. Copyright 2021, Elsevier. (D) Schematic illustration of the heterostructure  $\text{Co}-\text{Ni}_3\text{N}$  electrocatalyst for the conversion of PET plastic wastes [72]. Copyright 2022, Tsinghua University.



this case, the remaining photogenerated holes and electrons with strong redox capacities will remain in the original valence band or conduction band, so as to realize the spatial separation of active sites for the redox reactions. The accelerated charge transfer kinetics and the spatial separation of active sites caused by the Z-scheme heterojunctions both contribute to the efficient photocatalytic transformation of plastic wastes [78]. For example, Li et al. designed a self-assembled V-phosphomolybdic acid clusters/g-C<sub>3</sub>N<sub>4</sub> nanosheets (VPOM/CNNS) Z-scheme heterojunction photocatalyst according to the above considerations [79]. In the photocatalytic transformation of polyolefin and polyvinyl chloride plastic wastes into valued formic acid products, VPOM moiety with Keggin structure can not only realize reversible multi-electron redox transformation process, but also realize C-C bond catalytic cleavage over the vanadium atoms with variable valence states through an electron transfer-oxygen transfer pathway, as shown in Fig. 5B. In addition, the construction of Z-scheme heterojunctions can effectively alleviate the inherent high recombination rate in the VPOM materials, thus achieving a high photocatalytic conversion efficiency under the mild conditions [79]. In another successful attempt, Zhai et al. prepared a Cu<sub>7</sub>S<sub>4</sub>/CdS Z-scheme hetero-structured photocatalyst via a cation exchange method and successfully employed the composite photocatalyst to the photo-reforming of polylactic acid plastic wastes for the hydrogen generation, in which Cu<sub>7</sub>S<sub>4</sub> is proved to be a better co-catalyst than NiS or MoS<sub>x</sub> for the hydrogen evolution reaction [80]. The photocatalytic system has undergone three generations by reforming from liquid-phase biomimetic Z-scheme to all-solid-state Z-scheme and then to direct Z-scheme. The reformation gradually overcomes the engineering problem of being only applicable in solution phase, and the synthesis problem not being able to guarantee the accurate location of metal conductor between two semiconductors [81]. Even so, the research on the direct Z-scheme photocatalytic system is still need to investigate the detailed reaction mechanism and optimization strategy.

### 3.2. Constructing conductor-SEMI heterojunction

Another effective means of creating regions of space charge separation is constructing conductor-semiconductor heterojunctions, as shown in Fig. 4C. The conductors here include both metallic/quasi-metallic materials and carbon-based materials with high electrical conductivity. Metal-semiconductor heterojunction is also known as Schottky junction, the Fermi level differences between metal and semiconductor can induce the formation of the Schottky barrier, serving as an effective electron trap extracting photogenerated electrons from the semiconductor to promote the separation of photogenerated charge carriers [82]. In addition, loading noble metals can also improve the light absorption capacity of semiconductors through the surface plasmon resonance effect, especially in the visible and near-infrared light regions [83]. Besides, the introduction of quasi-metallic materials such as metal phosphides or sulfides can further render the Gibbs free energy for H of the catalytic system close to zero, which is conducive to the adsorption and desorption behaviors of hydrogen [84,85]. By contrast, carbon-based materials (carbon nanotubes, graphene, etc.) can not only promote the effective transfer of photogenerated electrons from semiconductors to carbon-based materials through the formation of Schottky barrier, but also provide a large number of surface active sites for heterogeneous reactions via the Langmuir-Hinshelwood mechanism, benefiting from their unique low-dimensional structure, high conductivity, superior electron mobility and storage capacity, and high specific surface area. The accelerated charge transfer kinetics caused by conductor-semiconductor heterojunctions is conducive to improve the photocatalytic conversion efficiency of plastic wastes [86]. For example, in order to ameliorate the inherent severe electron-hole recombination in the g-C<sub>3</sub>N<sub>4</sub> semiconductor and facilitate the hydrogen production in the photo-reforming process, Huang et al. and Huang et al. respectively introduced carbon nanotubes (CNTs) and reduced graphene oxide (rGO)

onto the g-C<sub>3</sub>N<sub>4</sub> material to form the Schottky barrier [87,88]. In addition to the Fermi level difference mentioned above leading to the fast electron transfer kinetics, the strong  $\pi$ - $\pi$  interaction between low-dimensional carbon-based materials can also promote the electron transport and improve the lifetime of photogenerated carriers. With the assistant of Ni-Mo alloy and Ni<sub>x</sub>Co<sub>1-x</sub>P metal phosphide cocatalysts for the hydrogen evolution reaction, the above heterojunctions have been successfully utilized in the photo-reforming of polyester plastic wastes, in which the carbon-based material can be regarded as an excellent electron transport medium between the g-C<sub>3</sub>N<sub>4</sub> light-absorbing layer and the cocatalysts for the hydrogen evolution reaction, as shown in Fig. 5C [87,88].

In general, the underlying mechanism of constructing semiconductor-based heterojunctions can be attributed to effectively regulate the interfacial charge transfer by inducing the directional transportation of photogenerated charge carriers, so that the depressed carrier recombination rate and the increased solar-to-chemical conversion efficiency can be reached. Considering that the existing works on the plastic photo-reforming mainly focus on designing cocatalysts for the hydrogen evolution reaction, more emphasis should be placed on the decoration of cocatalysts for the selective transformation of plastic wastes into valued chemicals. In this case, the heterojunction photocatalysts with the rational modification of multifunctional cocatalysts can be used for the photocatalytic transformation of plastic wastes with high catalytic activity and selectivity.

### 3.3. Constructing heterostructure electrocatalysts

For electrocatalytic transformation of plastic wastes, the interfacial charge transfer regulating strategy is mainly realized by constructing heterostructured electrocatalysts [89]. A typical heterostructured electrocatalyst is composed of two components placed to each other by the well-defined interfaces, but differing in the chemical composition and the crystal structure, as shown in Fig. 4D. The electronic interactions and the electron redistribution can be attributed to the interfacial electron migration driven by the differences in electronegativity or work functions of different components. They help to regulate the electron density around the active sites so as to reduce the adsorption and activation energy of the reactive substrates under working conditions [90]. Moreover, constructing heterostructured electrocatalysts also presents the following merits: (1) the confinement effect facilitates preventing the nanostructured materials from the agglomeration phenomena as well as accommodating and stabilizing the sufficient active sites; (2) the lattice strain effect and the interface bonding effect caused by the structural distortion at the interface of the two components contribute to the formation of the active sites and the regulation of the electronic structure; and (3) the synergistic effect of the physicochemical properties of the two components can promote the catalytic activity and stability of the overall heterostructured electrocatalyst. To integrate the above advantages of constructing heterostructured electrocatalyst, Huang et al. and Chen et al. fabricated the various transition metal nitrides heterostructured electrocatalysts, respectively [72,91,92]. Specifically, the bifunctional Co-Ni<sub>3</sub>N electrocatalysts exhibited an excellent electrocatalytic activity for the hydrogen evolution reaction, as well as an extremely high electrocatalytic oxidation activity of PET hydrolysate, providing a promising prospect for the electrocatalytic coupling systems to coproduce the valued chemicals and clean hydrogen fuels, as shown in Fig. 5D [72]. Although the construction of heterostructured electrocatalysts has undergone extensive progress on the transformation of plastics, the research is still in its infancy and faces a lot of challenges in the future. For example, the stability of the well-defined heterostructured interfaces under working conditions is one of the problems remain to be resolved.

#### 4. Morphological structure regulation

The photo- /electro-catalytic process focuses on the reactant conversion occurring at the catalyst surface, whose activity is related to the specific surface area and the density of active sites [93]. In general, reducing the particle size of a photocatalyst or an electrocatalyst will not only increase its surface-to-volume ratio to expose more active sites, but also significantly shorten the charge transport distance from bulk to surface to accelerate the charge transfer kinetics. In recent years, the regulation of morphological structure and properties as well as the structure-performance relationship have drawn increasing attention in the field of photo- /electro-catalytic transformation of plastic wastes, and the widely investigated morphological structure regulating strategy can be mainly divided into constructing multidimensional nanostructure and porous nanostructure, as shown in Fig. 6.

##### 4.1. Constructing multidimensional nanostructure

Multidimensional nanostructure is generally smaller than 100 nm in at least one dimension, including zero-dimensional (nanoparticles and quantum dots), one-dimensional (nanotubes and nanowires), two-dimensional (nanosheet and nanoflake) and three-dimensional (hierarchical nanostructures) structures [94]. The catalytic activity of catalysts is closely related to their microscopic morphological and structural features. The photocatalyst or electrocatalyst with multidimensional-architecture generally show distinctive physicochemical properties and catalytic performance from their bulk counterparts. In general, catalysts with multidimensional nanostructures possess higher specific surface areas, expose more active sites, have abundant diffusion space conducive to mass transfer of reactants/products, and have favorable transport pathways beneficial to the charge transfer from bulk to surface [94]. In particular, because of the quantum confinement effect caused by the reduced dimension, the regulation of semiconductor nanostructure also has an important effect on the energy band structure, which further influences the light absorption ability of photocatalyst (forbidden band width), separation and transportation of photo-generated charge carriers (band bending) and redox capacity of photo-generated electrons and holes (band edge position), etc [95–97].

**Photocatalysis.** Multidimensional nanostructured photocatalysts can efficiently catalyze the transformation of plastic wastes by the virtue of their excellent electronic, optical and surface properties. For example, zero-dimensional semiconductor quantum dots present a series of advantages, including the high extinction coefficient in the solar spectrum, the size-dependent band structure due to quantum confinement effect, the high surface-to-volume ratio for abundant active sites, and the feasibility of surface modification or passivation [95]. Specifically, Reisner et al. first prepared ligand-free CdS quantum dots, which can form a stable  $\text{Cd}(\text{OH})_2/\text{CdO}$  ( $\text{CdO}_x$ ) passivation layer at the surface in a strongly alkaline environment [98]. Mechanistic studies show that the passivation layer can reduce the surface defect sites to inhibit the non-radiative recombination, and also allow the tunneling of photo-generated charge carriers from the core-shell interface to the solution. In addition, the formation of analogous  $\text{CD}-\text{O}-\text{R}$  bonds can promote the effective binding between the quantum dot photocatalyst and the reaction substrate and accelerate the oxidative transformation of the reaction substrate. The CdS quantum dots were successfully utilized for the photoreforming of lignocellulose and polyester plastics to produce clean hydrogen fuel, as shown in Fig. 7A [98].

Additionally, two-dimensional semiconductor nanosheets usually have atom-level thickness and large lateral dimensions, the resulting high specific surface area contributes to support the active sites and guarantee the mass transfer and surface accessibility of reaction substrates [97]. Moreover, the exposed coordinatively unsaturated atoms or dangling bonds at the surface and edge of the nanosheets can also govern the adsorption, stabilization, desorption and other dynamic behaviors of key intermediates [97]. Considering the above superiorities, Sun et al. successively employed a single-unit-cell thick  $\text{Nb}_2\text{O}_5$  layer photocatalyst (Fig. 7B), an in-plane hetero-structured  $\text{NiO}/\text{Fe}_2\text{O}_3$  nanosheets photocatalyst and a  $\text{Co}-\text{Ga}_2\text{O}_3$  nanosheet photocatalyst to realize the photocatalytic oxidative cleavage of C–C bonds within plastic wastes into inorganic small molecule  $\text{CO}_2$  and/or a continuous photo-reduction process of  $\text{CO}_2$  to produce  $\text{C}_2$  fuel or syngas [54,99,100]. The authors also highlighted the  $\text{CO}_2$  photoreduction is the rate-limiting step in the above transformation process.

**Electrocatalysis.** Multidimensional nanostructured electrocatalysts with superior electronic and surface properties than their bulk counterparts have also raised significant research upsurge in the electrocatalytic transformation of plastic wastes. For instance, constructing one-dimensional nanowires or nanorods electrocatalysts is conducive to the high electrocatalytic activity, mainly owing to the higher aspect ratio for more accessible active sites, the well-defined exposed crystal facets and defects to boost the charge transfer kinetics, and the decoupled light penetration length and charge transport pathway giving a high incident-light utilization efficiency (mainly suitable for photo-electrodes) [96]. Specifically, Zhao et al. reported an electrocatalytic valorization of PET plastics using  $\text{CuO}$  nanowires (NWs) catalyst, and highlighted the possible oxidation pathway of PET-derived EG molecules involving the generation of glyoxal intermediates and the oxidative cleavage of C–C bonds to form valued formic acid, as shown in Fig. 7C [101]. They also synthesized the  $\text{Fe}_2\text{O}_3$ -based nanoworm-like photoanodes and achieved the photoelectrochemical catalysis of PET plastic wastes into the target product of formic acid with the help of  $\text{Ni}(\text{OH})_x$  cocatalyst [102]. The one-dimensional nanostructures of (photo)electrodes were proved to meet well the demands of charge and mass transfer for the effective transformation of plastic wastes. Additionally, the anodic electrooxidation of PLA plastic wastes into valued acetic acid coupled with the cathodic hydrogen evolution reaction was realized by using a bifunctional  $\text{CoSe}_2$  electrocatalyst, benefiting from the ultrathin thickness, abundant edge active sites, and large electrochemical active area of the two-dimensional nanostructure [71].

Overall, constructing multidimensional nanostructure strategies have been demonstrated as a key approach to implement the effective photo- /electro-catalytic transformation of plastic wastes. The favorable charge transfer from bulk to surface and mass transfer within the

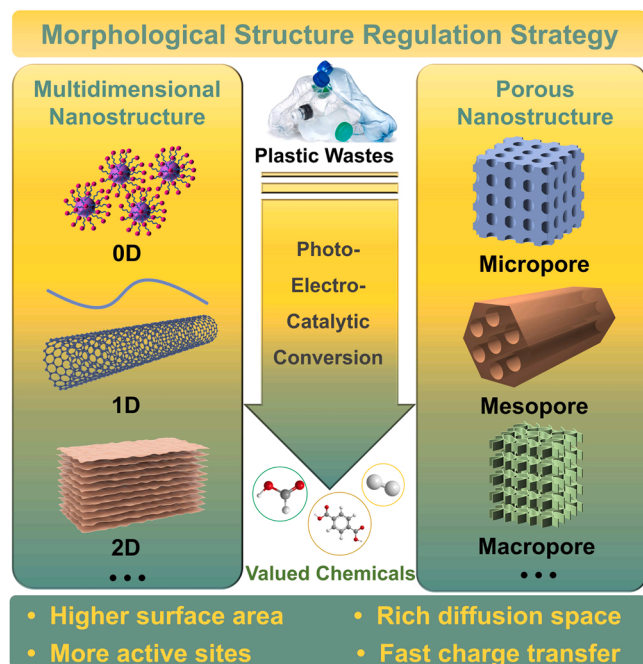
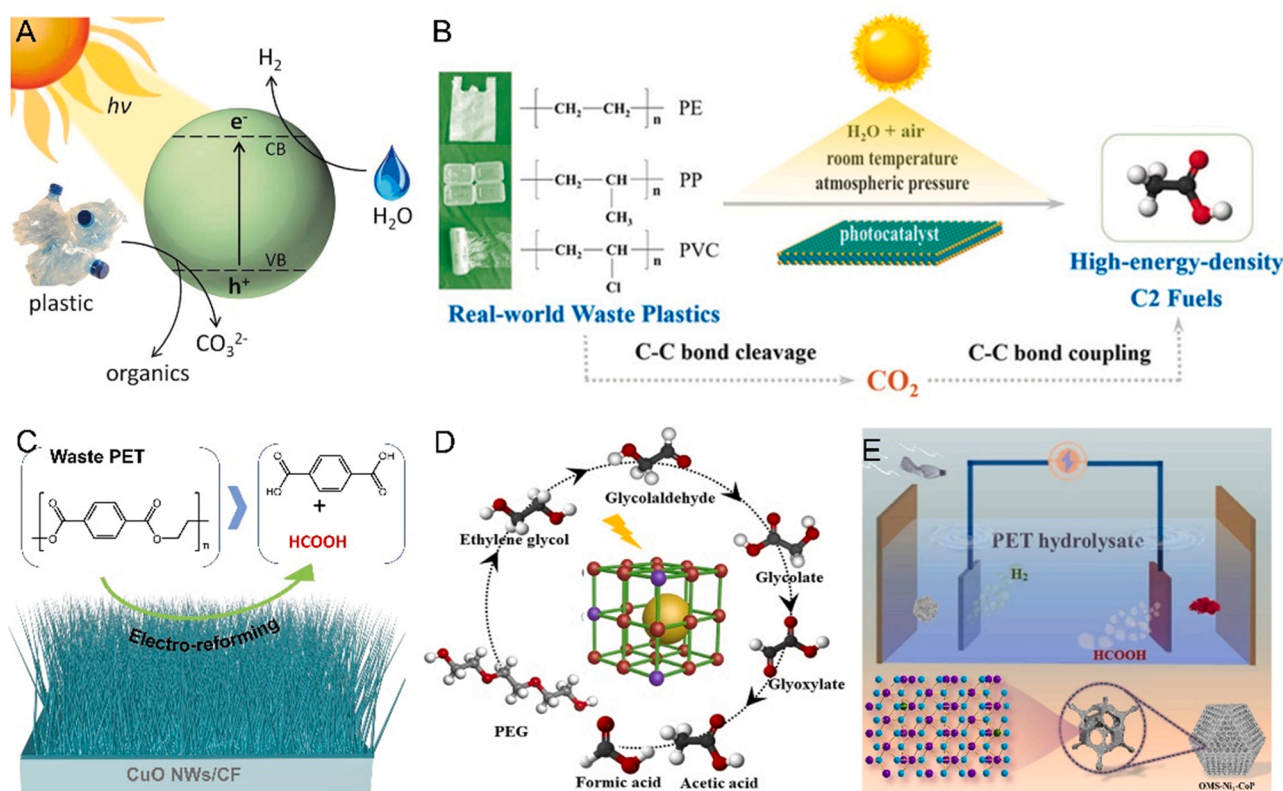


Fig. 6. Schematic illustration of morphological structure regulation strategy for the photo- /electro-catalytic transformation of plastic wastes.



**Fig. 7.** (A) Diagram of the plastic photo-reforming process with a CdS/CdO<sub>x</sub> quantum dot photocatalyst. [98] Copyright 2018, The Royal Society of Chemistry. (B) Schematic illustration for converting various waste plastics into C<sub>2</sub> fuels by a two-step pathway under simulated natural environment conditions [99]. (C) Electro-reforming of PET plastic to produce valued chemicals by using CuO NWs electrode [101]. Copyright 2022, The American Chemical Society. Copyright 2020, Wiley-VCH GmbH. (D) The possible photocatalytic conversion pathway of PEG by Ag<sub>2</sub>O/Fe-MOF photocatalyst with porous structure [104]. Copyright 2022, Elsevier. (E) Schematic illustration of the HER//PETOR pair-electrolysis system based on bifunctional ordered macroporous superstructure Ni<sub>1</sub>-CoP electrocatalyst [105]. Copyright 2022, Elsevier.

interspace of nanoarchitectures synergistically contribute to the improved catalytic activity. The balance between the catalytic activity and long-term stability calls for more attention for the future fabrication of photocatalysts and electrocatalysts.

#### 4.2. Constructing porous nanostructure

Introducing rich porosity into photo-/electro-catalytic materials is widely used as an efficacious strategy to endow them with some specific optoelectronic and electronic functionalities. Porous nanostructure contains multi-level pores, covering microporous (< 2 nm), mesoporous (2–50 nm) and macroporous (> 50 nm) structures, can provide the mobile guest species with abundant active sites in various applications such as adsorption, separation, storage, energy conversion and catalytic reaction throughout the internal and external space of the pores and channels [103]. Compared with multidimensional nanostructures, photocatalysts and electrocatalysts with porous nanostructures generally possess high specific surface area, adjustable pore size and pore wall thickness, and interconnected porous networks, which are conducive to the mass transfer of reactive substrates towards the active sites within the channels, and also contributes to the adsorption/desorption behaviors of the reactive substrates onto/from the active sites.

**Photocatalysis.** The advantages of photocatalysts with porous nanostructure mainly lie in the following four aspects: (1) the multiple scattering of incident light by pore structure can improve its light absorption capacity; (2) the nanoscale particle size and pore wall thickness can shorten the charge transfer distance to promote the separation and transportation of photogenerated charge carriers; (3) the spatially

distributed co-catalysts, loading on the inner and outer surfaces of the pores respectively, can induce additional built-in electric fields in the radial direction of the pore structure, further accelerating the directional charge transfer dynamics; (4) the higher specific surface area can increase the active center density and the mass transfer efficiency of the reactive substrate [106]. Among the various photocatalysts with porous nanostructure, metal-organic frameworks (MOFs) as a representative are composed of rigid multipodal organic linkers and metal ions or clusters of metal ions nodes. Structural characteristics of MOFs including crystallinity and porosity render them with high pore volume, specific surface area, and low framework density [107]. To improve the catalytic activity of MOFs for the photocatalytic plastic transformation and make full use of their complicated pore structure, Zhang et al. adopted an in-situ photochemical method to prepare a p-n type heterogeneous photocatalyst with ultra-small-sized Ag<sub>2</sub>O nanoparticles uniformly dispersed in Fe-MOF pore structure [104]. The photocatalyst mentioned above was successfully applied to the photoreforming of plastic wastes such as PE and PET by virtue of the abundant active sites supported by the large surface area, and the enhanced separation and transportation efficiency of photogenerated charge carriers brought by the built-in electric field of heterojunction, as shown in Fig. 7D [104].

**Electrocatalysis.** Porous materials with abundant channels and ample voids are also particularly advantageous for the electrocatalytic plastic transformation. The efficient surface behaviors and mass transfer of reactants depend on the accessibility active sites, which can be implemented by constructing porous nanostructure within electrocatalysts [108]. For example, Zhu et al. fabricated an OMS-Ni<sub>1</sub>-CoP electrocatalyst from the ordered macroporous ZIF-67 single crystals, featuring distinctive structural advantages provided by its ordered



macroporous superstructure with abundant built-in mesopores [105]. The bifunctional electrocatalyst can be employed for both the cathodic hydrogen evolution reaction and the anodic PET electrocatalytic conversion in a coupling system, as shown in Fig. 7E. The high porosity and large specific surface area play a vital role on the electrocatalytic conversion of PET-derived EG into FA on the  $\text{Ni}_1-\text{CoOOH}$  active sites formed by the electrochemical reconstruction of metal phosphides [105].

Constructing porous nanostructure is a promising complementary strategy for the surface-dominated heterogeneous photo-/electro-catalytic transformation of plastic wastes. However, a few of challenges still exist in this research field. For instance, the porous structure tends to collapse during the cyclic catalytic process, resulting in an inferior long-term stability. Although the above problem can be solved by thickening the pore wall, this will inevitably lengthen the charge transfer distance to decrease the conversion efficiency. Such challenges deserve more elaborate design for the porous nanostructures.

## 5. Catalytic system design

The above-mentioned photo-/electro-catalytic systems are mainly powered by the single energy input, either solar energy or electric energy. Despite these successful practices, the shortages of single catalytic technology may restrict future up-scaling applications. In addition, the surface-dominated heterogeneous photo-/electro-catalytic processes are closely related to the reactant diffusion and surface properties of catalysts, further improvement of the catalytic activity as well as selectivity still faces great challenges. Considering these limitations, the distinctive photo-/electro-catalytic system design strategy has been gradually proposed for the transformation of plastic wastes, including the construction of integrated heterogeneous catalytic systems to optimize the energy supply, and the construction of homogeneous catalytic systems to enhance the catalytic performance.

### 5.1. Integrated heterogeneous catalytic system

Various catalytic techniques, such as, electrocatalysis, photocatalysis, thermocatalysis and biocatalysis, have been widely developed for the transformation of plastic wastes [13,119]. Inspired by the coupling technologies in conventional catalytic-driven reactions, integrated catalysis combines the advantageous aspects of various technologies may promote the photo-/electro-catalytic transformation of plastic wastes. The interdisciplinarity can introduce the high conversion rate and scalability of thermocatalysis and the high specificity and biomimetic features of biocatalysis into photo-/electro-catalysis with high efficiency and selectivity under mild reaction conditions. In recent years, photothermocatalysis and photoelectrocatalysis are two most commonly integrated catalytic systems for the transformation of plastic wastes.

Recently, solar energy has been complementary to thermal energy to synergistically drive the catalytic transformation of plastic wastes. Specifically, Chen et al. have proposed a sustainable and efficient solar-thermal catalytic upcycling strategy for transforming polyester plastics to high-value monomer derivatives using polydopamine-modified commercial multi-walled carbon nanotubes, as shown in Fig. 8A [109]. Benefiting from the unique localized heating effect, the conversion efficiency and product yield of solar-thermal catalysis are three-fold higher than those of thermal catalysis under similar conditions. Lately, Chen et al. further integrated cobalt single-site catalysts (Co SSCs) with CNT-PDA as the photothermal reagent to elevate the accessibility of heterogeneous catalysts. The favorable nucleophilic addition elimination processes promoted by the coordination-unsaturated  $\text{Co}-\text{O}_5$  single-sites gave rise to an 82.6 % BHET yield in three-hour photothermal glycolysis of PET plastic [110]. The validated universality, selective-recycling capability, scalability and stability of solar-thermal catalysis make it valuable for future

industrial applications [109]. An integration of solar and thermal catalysis can optimize the energy supply, while photocatalysis and electrocatalysis can be combined to enhance the efficiency and selectivity of the process.

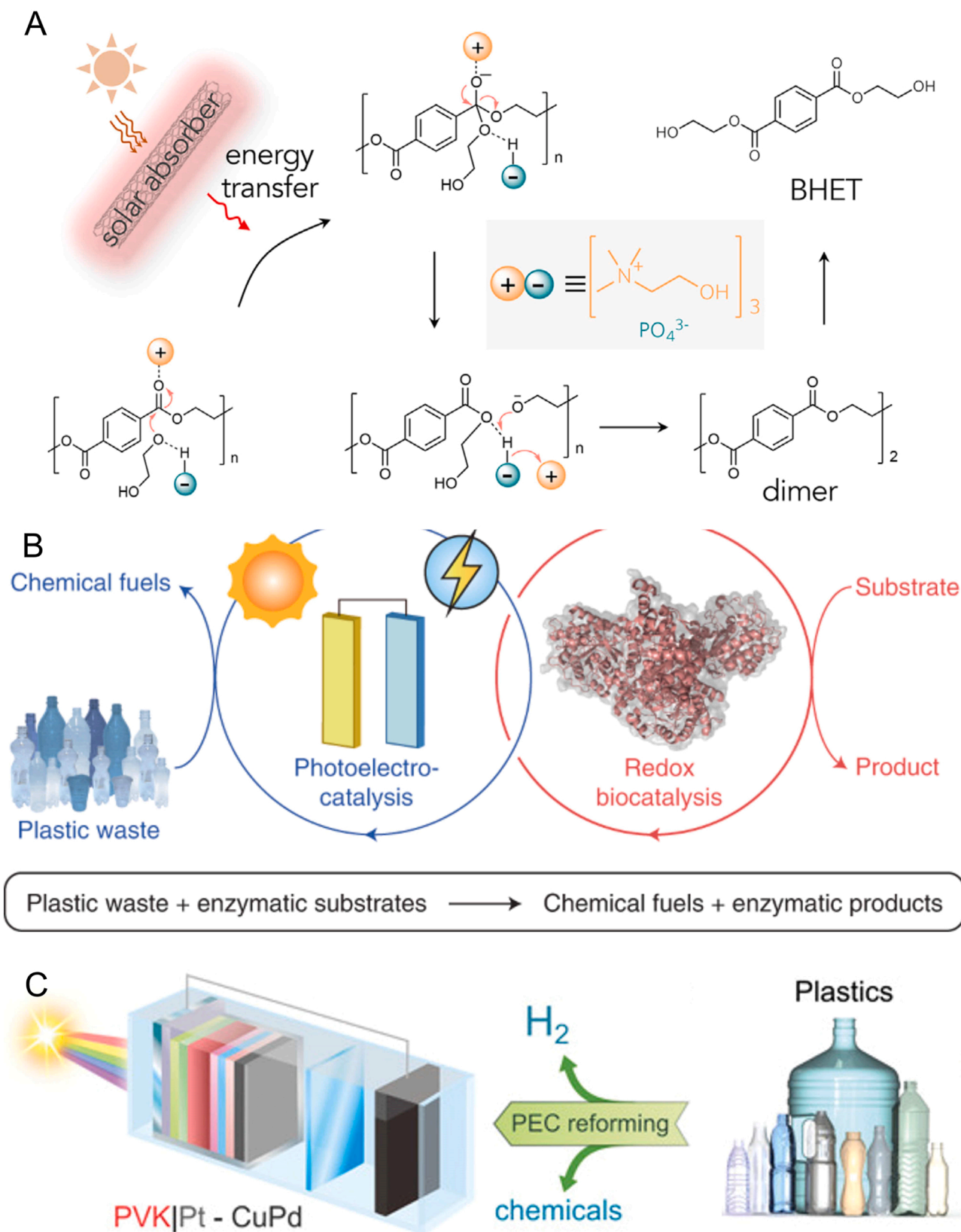
Additionally, a photoelectrochemical configuration consisting of separated compartments is conducive to decoupling oxidation and reduction half-reactions to maximize the value output. Lin et al., Zhao et al. and Park et al. successively fabricated the photoanodic PET transformation systems coupled with cathodic hydrogen evolution reaction as well as redox enzyme-based biosynthesis (including oxy-functionalization of C-H bonds, amination of C=O bonds and asymmetric hydrogenation of C=C bonds, Fig. 8B) [102,111,112,120]. Besides, the anodic PET transformation or biomass reforming can also be combined with photocathodic hydrogen generation or  $\text{CO}_2$  reduction by a perovskite-based photocathode or an assembly of "artificial leaf" configuration, as shown in Fig. 8C [29,121,122]. From an economic and environmental perspective, integrated catalytic systems for plastic transformation are high-performance, high-profit, and eco-friendly methods which not only contribute to fundamental theoretical research, but also exhibit appealing potential industrial prospects. Future research should focus on multifunctional materials with photothermal, photoelectric, and/or thermoelectric properties for the closed-loop chemical transformation of plastic wastes. Furthermore, the influence of additives on the reactivity and durability of catalysts in real-life plastic manufacturing should be investigated. Finally, light absorption, heat transfer, and mass transfer should be considered during the construction of large-scale equipment.

### 5.2. Homogeneous catalytic system

Heterogeneous catalysis, in which the reactant and catalyst are in different phases, is mainly triggered after reactant adsorption and activation on the catalyst surface. The reactant molecules must diffuse from the gas or liquid phase to the solid catalyst surface [123]. Hence, the influence of diffusion process on the reaction kinetics should be emphasized in many cases. Compared with heterogeneous catalysis, homogeneous catalysis may not involve the surface heterogeneity and internal/external diffusion limitation of solid catalysts, so it is easier to get insight into reaction kinetics and working mechanisms in homogeneous systems. Moreover, homogeneous catalysis is independent of the interphase diffusion, causing a higher reaction rate and product selectivity than those of heterogeneous catalysis [124]. Given this, homogeneous catalysis will offer unique possibilities for the photocatalytic transformation of plastic wastes. In this case, the limited conversion efficiency of heterogeneous transformation caused by the insolubility of plastic polymer and catalyst in the aqueous phase can be significantly ameliorated.

In earlier studies, in order to achieve a more controllable light-driven transformation process, researchers usually incorporate some specific functional groups (such as the hydroxyl group) onto the polymer skeleton to induce the effective cleavage of adjacent C-C bonds [32, 113]. The transformation of the above functionalized plastic derivatives can provide an important reference for the transformation of real-world plastic wastes. In this manner, the hydroxylated polymer and photocatalyst (Ir and V-based complex catalysts) need to be fully dissolved in the appropriate organic solvent firstly. Upon the incident irradiation, the hydroxyl group is activated to form the reactive alkoxy group via the proton-coupled electron-transfer process. And then the C-C bond adjacent to the alkoxy group will take a rapid  $\beta$ -scission step to generate a carboxyl group and an alkyl group to be further hydroxylated. The well-defined and isolable small-molecule carboxylic acid products can be obtained by the continuous free-radical chain-reaction [32,113].

Compared with the hydroxylation of polymer chains, direct C-H bond activation is more challenging but more applicable to the ubiquitous plastics. Recently, researchers have paid more attention on the



**Fig. 8.** (A) Schematic representation of the upcycling PET plastic wastes by solar-thermal catalysis [109]. Copyright 2022, Elsevier. (B) Schematic diagram of solar-powered photoelectrochemical biosynthetic reactions for the transformation of non-recyclable real-world PET plastic wastes [112]. Copyright 2022, Springer Nature. (C) Schematic illustration of the Cu<sub>30</sub>Pd<sub>70</sub>/perovskite/Pt system for the upcycling of plastic wastes to produce H<sub>2</sub> and valued chemicals by photo-electrocatalysis technology [29]. Copyright 2021, Wiley-VCH GmbH.

photocatalytic homogeneous transformation of plastic wastes by the direct C–H bond activation [35,45,114,117]. By using hydrogen atom transfer (HAT) catalyst, C–H bond is activated to form an organic carbon-centered radical, which further reacts with oxygen molecules to generate an organic peroxy radical intermediate. The remaining C–H bond of the intermediate can be further activated for the cleavage to obtain a carbonyl group. Notably, if there exists no extra hydrogen atom in the intermediate, the adjacent C–C bond will process a rapid  $\beta$ -scission step to obtain carboxylic acid product [35,45]. The above working mechanism meets well the demands of photocatalytic transformation of polyolefin plastics containing tertiary carbon atoms, as shown in Fig. 9. Previous studies have demonstrated that  $\text{FeCl}_2$  [114],  $\text{FeCl}_3$  (providing  $\text{Cl}\cdot$  radicals) [35], N-bromosuccinimide (NBS) (providing  $\text{Br}\cdot$  radicals) [116], acid [45] and aromatic ketone (providing singlet oxygen,  $^1\text{O}_2$ ) [117] can act as HAT photocatalysts to achieve selective homogeneous conversion of the polystyrene plastic into valued benzoic acid products. The resulting benzoic acid can further undergo the decarboxylation, hydroxylation or other tandem transformation to produce other valued products (e.g., benzene, diphenyl, toluene, etc.) [125]. In order to promote the HAT process, some pre-catalysts are usually introduced into the reaction system. For example,  $\text{CF}_3\text{SO}_2\text{Na}$  can in situ generate pentacoordinate sulfide containing hexavalent sulfur under photocatalytic conditions to enhance the HAT efficiency of NBS, as shown in Fig. 9. [116] 2,2,2-trichloroethanol ( $\text{CCl}_3\text{CH}_2\text{OH}$ ) can produce alkoxy radicals to participate in the HAT process together with chloride radicals from  $\text{FeCl}_3$ . [115] The universality, practicability and scalability of the above strategies have also been demonstrated, showing potential for the transformation of PE, PP and PVC. More importantly, the concept of C–H activation and C–C scission can also extend to the photocatalytic heterogeneous system [118].

Although the construction of homogeneous catalytic system can significantly improve the conversion rate and selectivity of plastic reactants in a more universal and scalable manner, its future development in the plastic transformation also faces some challenges. The first problem comes from the separation and recovery of reaction products and catalysts from the homogeneous phase, which tends to raise the

operating cost and complexity. Secondly, the physicochemical properties of metal complex organocatalysts can be regulated by changing the ligand components, however, the complex synthetic process may not meet the needs of the large-scale manufacture. Finally, the potential health and environmental hazards caused by the organic catalysts and solvents also limit their long-term development in the future.

## 6. Summary and outlook

Numerous policies and technologies have been developed to alleviate the environmental impact caused by plastic wastes. In addition to conventional plastic wastes disposal methods, photo-/electro-catalytic technology provides a promising “waste-to-wealth” route to transform polymer waste into valued chemicals and fuels under mild conditions. Currently, the photo-/electro-catalytic conversion strategies have been investigated to utilize the latent value of plastic wastes to generate valuable chemicals (such as, hydrogen, formic acid, and other hydrocarbons). Moreover, photo-/electro-catalytic transformation processes exhibit higher economic and ecological value than traditional treatment methods due to the utilization of renewable energy and the rational design of earth-abundant transition metal-based catalysts and appreciation catalytic systems. Table 1 have summarized the different regulation strategies for the valorization of plastic wastes by photo-/electro-catalysis technology.

Although various reports on the transformation of plastic waste using photo-/electro-catalytic technologies, there are still many challenges to be overcome before large-scale production and commercial applications.

First, more efficient photo-/electro-catalysts with high activity, stability, and selectivity should be rationally designed and developed for the selective cleavage of chemical bond in the polymer chains to produce valued chemicals and fuels. The reaction route and catalytic mechanism of plastic waste conversion also require future investigation; this could inspire the novel design routes of catalysts in the future. The design and utilization of upscaling reactors (e.g., fluid flow reactors) is of great significance for future industrial applications. The effects of technological parameters (such as, light transmission, electroconductivity and

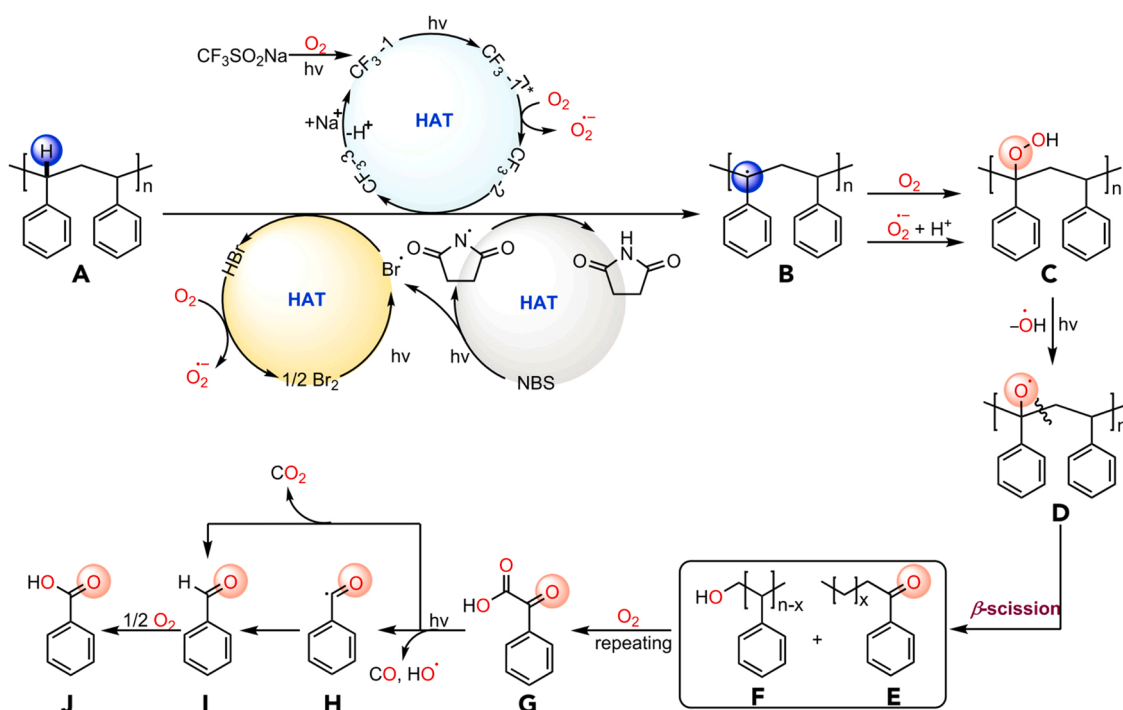


Fig. 9. Reaction mechanism for the transformation of polystyrene plastic wastes into benzoic acid by homogeneous catalysis. [116] Copyright 2022, Elsevier.



**Table 1**

Summary of the catalyst and catalytic system design strategy for the conversion of plastic polymers by sustainable catalysis technology.

Catalysts	Technology	Conditions	Performances	Ref.
<b>Electronic structure regulation</b>				
Co–Ga <sub>2</sub> O <sub>3</sub>	Photocatalysis	Xe lamp, AM 1.5 G, 100 mW/cm <sup>2</sup> , Water	PE: 647.8, 158.3 and 419.3 μmol g <sup>−1</sup> h <sup>−1</sup> productivity for H <sub>2</sub> , CO and CO <sub>2</sub>	[54]
C, N – TiO <sub>2</sub>	Photocatalysis	50 W LED, λ = 400 – 800 nm, pH 3, 0 °C	HDPE: Average mass loss of 71.77 ± 1.88% in 50 h	[53]
BS <sub>x</sub> –CN	Photocatalysis	Xe lamp, λ > 420 nm, 1 M KOH, 10 °C	PLA: 18.90 mmol g <sup>−1</sup> h <sup>−1</sup> productivity for H <sub>2</sub> ; HCOOH and CH <sub>3</sub> COOH formation	[55]
MoS <sub>2</sub> /Zn <sub>0.5</sub> Cd <sub>0.5</sub> S	Photocatalysis	Xe lamp, AM 1.5 G, 10 M NaOH	PET: 15.90 mmol g <sup>−1</sup> h <sup>−1</sup> productivity for H <sub>2</sub> ; HCOOH and CH <sub>3</sub> COOH formation	[57]
MXene/ Zn <sub>0.6</sub> Cd <sub>0.4</sub> S	Photocatalysis	Xe lamp, λ > 420 nm, 10 M NaOH, 5 °C	PET: 14.17 mmol g <sup>−1</sup> h <sup>−1</sup> productivity for H <sub>2</sub> ; formation of glycolate and formate etc.	[64]
<sup>NCN</sup> CN <sub>x</sub> /Ni <sub>2</sub> P	Photocatalysis	Xe lamp, AM 1.5 G, 100 mW/cm <sup>2</sup> , 1 M KOH	PET/PLA: 1.65/3.56 μmol g <sup>−1</sup> h <sup>−1</sup> productivity for H <sub>2</sub> ; HCOOH and CH <sub>3</sub> COOH formation	[31]
<sup>NCN</sup> CN <sub>x</sub> /Ni <sub>2</sub> P	Photocatalysis	Xe lamp, AM 1.5 G, 0.5 M KOH, 25 cm <sup>2</sup> panel	PET: 52 μmol m <sup>−2</sup> h <sup>−1</sup> productivity for H <sub>2</sub> ; HCOOH formation	[70]
NiCo <sub>2</sub> O <sub>4</sub>	Electrocatalysis	1 M NaOH	PET: 90 % FE for HCOOH at 1.45 V <sub>RHE</sub>	[40]
CuCo <sub>2</sub> O <sub>4</sub>	Electrocatalysis	1 M KOH	PET: 93 % FE and 86 % selectivity for HCOOH at 1.5 V <sub>RHE</sub>	[56]
Pd	Electrocatalysis	10 M KOH	PET: 95 % FE and 93 % selectivity for K <sub>2</sub> CO <sub>3</sub> at 0.7 V <sub>RHE</sub>	[65]
Cu <sub>30</sub> Pd <sub>70</sub>	Electrocatalysis	1 M KOH	PET: 9.32 μmol h <sup>−1</sup> productivity, 88% FE and 91% selectivity for glycolic acid	[29]
CoNi <sub>0.25</sub> P	Electrocatalysis	1 M KOH	PET: 4.1 mmol cm <sup>−2</sup> h <sup>−1</sup> productivity and 91.7% FE for HCOOH at 1.7 V <sub>RHE</sub>	[26]
<b>Interfacial charge transfer regulation</b>				
CdO <sub>x</sub> /CdS/SiC	Photocatalysis	Xe lamp, AM 1.5 G, 10 M NaOH, 70 °C	PE: 25 μmol g <sup>−1</sup> h <sup>−1</sup> productivity for H <sub>2</sub>	[77]
VPOM/g–C <sub>3</sub> N <sub>4</sub>	Photocatalysis	Xe lamp, λ > 420 nm, CH <sub>3</sub> CN, 1 atm O <sub>2</sub> , R.T.	PE/PP/PVC: 24.66/26.68/29.85 μmol g <sup>−1</sup> h <sup>−1</sup> productivity for HCOOH	[79]
Cu <sub>7</sub> S <sub>4</sub> /CdS	Photocatalysis	Xe lamp, λ > 420 nm, 10 M NaOH	PLA: 21.62 mmol g <sup>−1</sup> h <sup>−1</sup> productivity for H <sub>2</sub>	[80]
Pt/TiO <sub>2</sub>	Photocatalysis	Xe lamp, white light, 5 M NaOH, R.T.	PE/PVA/PVC: 9.3/8.6/4.5 μmol h <sup>−1</sup> productivity for H <sub>2</sub>	[30]
CN–CNTs–NiMo	Photocatalysis	Xe lamp, 95 mW/cm <sup>2</sup> , 10 M KOH, 15 °C	PET: 90 μmol g <sup>−1</sup> h <sup>−1</sup> productivity for H <sub>2</sub>	[87]
Ni <sub>3</sub> Co <sub>1–x</sub> P/rGO/CN	Photocatalysis	Xe lamp, λ > 420 nm, 1 M KOH, 10 °C	PLA: 576.7 μmol g <sup>−1</sup> h <sup>−1</sup> productivity for H <sub>2</sub> ; HCOOH and CH <sub>3</sub> COOH formation	[88]
Co–Ni <sub>3</sub> N	Electrocatalysis	1 M KOH	PET: 92 % FE for HCOOH at 1.18 V <sub>RHE</sub>	[72]
Ni <sub>3</sub> N/W <sub>5</sub> N <sub>4</sub>	Electrocatalysis	1 M KOH	PET: 1.2 mmol cm <sup>−2</sup> h <sup>−1</sup> productivity, ~85% FE for HCOOH at 1.6 V <sub>RHE</sub>	[92]
<b>Morphological structure regulation</b>				
CdS/CdO <sub>x</sub>	Photocatalysis	Xe lamp, AM 1.5 G, 100 mW/cm <sup>2</sup> , 10 M NaOH, 25 °C	PLA/PET/PUR: ~64.3/12.4/3.22 mmol g <sup>−1</sup> h <sup>−1</sup> productivity for H <sub>2</sub>	[98]
Nb <sub>2</sub> O <sub>5</sub>	Photocatalysis	Xe lamp, AM 1.5 G, 100 mW/cm <sup>2</sup> , water, 25 °C	PE/PP/PVC: 47.4/40.6/39.5 μg g <sup>−1</sup> h <sup>−1</sup> productivity for CH <sub>3</sub> COOH	[99]
NiO/Fe <sub>2</sub> O <sub>3</sub>	Photocatalysis	Xe lamp, AM 1.5 G, 100 mW/cm <sup>2</sup> , water, 25 °C	PET: 3.7 mmol g <sup>−1</sup> h <sup>−1</sup> productivity, 100% selectivity for CO <sub>2</sub>	[100]
Ag <sub>2</sub> O/Fe–MOF	Photocatalysis	Xe lamp, AM 1.5 G, 100 mW/cm <sup>2</sup> , water, 25 °C	PEG/PET/PE: 2.48/1.7/1.9 mmol g <sup>−1</sup> h <sup>−1</sup> productivity for H <sub>2</sub>	[104]
CuO	Electrocatalysis	1 M KOH	PET: 85 % FE for HCOOH at 1.45 V <sub>RHE</sub>	[101]
CoSe <sub>2</sub>	Electrocatalysis	1 M KOH	PLA: 97 % FE for CH <sub>3</sub> COOH at 1.5 V <sub>RHE</sub>	[71]
OMS Ni <sub>1–x</sub> –CoP	Electrocatalysis	1 M KOH	PET: 96 % FE for HCOOH at 1.3 V <sub>RHE</sub>	[105]
<b>Catalytic system design</b>				
CNT–PDA	Photocatalysis	Xe lamp, 600 mW/cm <sup>2</sup> , EG, choline phosphate, 180 °C	PET: 100 % conversion efficiency and 82% yield for BHET	[109]
Co SSCs/CNT	Photocatalysis	Xe lamp, 740 mW/cm <sup>2</sup> , EG, 180 °C	PET: 100 % conversion efficiency and 82.6% yield for BHET	[110]
Ni–P/TiO <sub>2</sub>	Photocatalysis	Xe lamp, AM 1.5 G, 100 mW/cm <sup>2</sup> , 1 M KOH	PET: ~6.4 μmol productivity, 57.1% FE for HCOOH	[111]
Ni(OH) <sub>x</sub> /Fe <sub>2</sub> O <sub>3</sub>	Photocatalysis	Xe lamp, AM 1.5 G, 100 mW/cm <sup>2</sup> , 1 M KOH	PET: ~100 % FE for HCOOH at 1.2 V <sub>RHE</sub>	[102]
Zr: Fe <sub>2</sub> O <sub>3</sub>	Photocatalysis	Xe lamp, AM 1.5 G, 100 mW/cm <sup>2</sup> , 5 M NaOH	PET: ~530/185nmol productivity for HCOOH/ CH <sub>3</sub> COOH	[112]
V–based molecule	Photocatalysis	White LED, CD <sub>3</sub> CN/toluene–d <sub>8</sub> , air or O <sub>2</sub> , 85 °C	PE–monoalcohol: > 95 % conversion efficiency; formation of alkyl formates in 6 days	[113]
Ir–based molecule	Photocatalysis	Blue LEDs, TRIP thiol, Toluene, 35 – 40 °C	PMP–x/OTBS–x copolymer: 79 – 100%/29 – 77% yield for monomers	[32]
FeCl <sub>2</sub>	Photocatalysis	20 W LED, λ = 400 nm, DCM/MeCN, 1 atm O <sub>2</sub>	PS: 100 % conversion in 6 h, 63% yield for benzoic acid in 66 h	[114]
FeCl <sub>3</sub>	Photocatalysis	100 W Blue LEDs, λ = 390 nm, acetone, 1 atm O <sub>2</sub>	PS: 67 % yield for benzoic acid in 5 days	[115]
–Cl <sub>3</sub> CCH <sub>2</sub> OH	Photocatalysis	White LED, acetone, 1 atm O <sub>2</sub>	PS: 23 mol% yield for benzoyl products in 20 h	[35]
FeCl <sub>3</sub>	Photocatalysis	Kessil lamp, λ = 390 nm, ethyl acetate, 1 atm O <sub>2</sub>	PS: 73 % yield for benzoic acid in 16 h	[116]
NBS–CF <sub>3</sub> SO <sub>2</sub> Na	Photocatalysis	Violet–blue LEDs, λ = 405 nm, benzene/CH <sub>3</sub> CN, R.T.	PS: 67 %/50 % yield for HCOOH/benzoic acid in 15 h	[45]
pTsOH–H <sub>2</sub> O	Photocatalysis	Blue LEDs, H <sub>2</sub> SO <sub>4</sub> , ethyl acetate, 1 atm O <sub>2</sub> , 50 °C	PS: 30 ± 2 % yield for benzoic acid in 16 h	[117]
Fluorenone	Photocatalysis	Xe lamp, CH <sub>3</sub> CN, 10 bar O <sub>2</sub> , 150 °C	PS: 96 % conversion and 61 % selectivity for aromatic oxygenates in 24 h	[118]

mass transfer) on the overall efficiency of catalytically driven systems should be extensively investigated.

Second, the significance of techno–economic analysis and life cycle assessment on the photo–/electro–catalytic plastic transformation should be emphasized for the future practical applications. The key indicators, such as the cost of developing catalysts and catalytic electrode, the optimized parameters of the up–scaling reactors, the cost of

constructing and operating a pilot plant, the expected energy returned on energy invested, and the possible environmental influence or process sustainability, etc, need to be considered to evaluate the economic and environmental feasibility of photo–/electro–catalytic plastic transformation processes. Considering the proof of concept of the current catalytic processes, the techno–economic analysis and life cycle assessment can clearly point out the future research directions of the

photo-/electro-catalytic technology for the alleviation of plastic pollution problems.

Third, efficient and stable catalytic system and reactor should be developed for scale up of the process. In addition, current electro-catalysis research focuses on converting plastic wastes into valued chemicals and hydrogen fuels using polyester plastics. The utilization of more robust polyolefin plastics should be emphasized in the future. Normally, photo-/electro-catalytic conversion processes for the plastic wastes require the pretreatment with strong acidic and basic solutions, which increase the equipment operation and maintenance challenges. The indirect conversion strategies always need to firstly decompose plastic wastes into water-soluble small organic molecules and then transform them into valued chemicals by photo-/electro-catalysis. Given this, the reported studies that photo-/electro-catalysis selectively oxidize or reduce small organic molecules into valued chemicals can be used to inspire new insights for the valorization of plastic waste [126]. Compared with indirect conversion strategies, more facile direct conversion strategies also need to be developed. Recently, McNeil et al. developed a direct electrocatalysis conversion strategy for the valorization of PVC plastic wastes, which should inspire other direct conversion strategies for upcycling plastic wastes [127]. During the conversion process, chloride anions generated from PVC under electroreductive conditions could be directly used in a tandem electro-oxidative chlorination reaction. Therefore, A more facile and environment-friendly treatment process and direct conversion strategies should be explored developed in the future.

Fourth, real-life plastic wastes always contain a mixture of plastic types other than a single type of plastic, which will increase the operation difficulty by photo-/electrochemical methods. Normally, the mixed plastic wastes are sorted and then proceed for recycling in the traditional methods. Given that the activity and component of the photo-/electro-catalysts can be regulated, more efficient catalysts and catalytic systems possess multifunctional features with high stability should be developed for the transformation of mixed-plastic wastes into valued chemicals or fuels in the future.

Fifth, miscellaneous endogenous additives are usually added to commercial plastics to enhance their properties during the manufacturing process, and complex exogenous contaminants are involved in the production of real-life plastic wastes. Normally, these additives and contaminants affect the activity, selectivity, and stability of catalysts, the efficiency of catalytic systems, and product purity. These effects on the transformation processes should be comprehensively investigated in the future.

Finally, the integrated catalytic technologies, combining the individual advantageous aspects of photocatalysis, electrocatalysis or other catalysis technologies, are still incompletely explored and utilized for the valorization of plastic wastes. The development of multifunctional catalysts involving superior photoelectric, photothermal and thermo-electric performances should be a priority in follow-up researches. It is also vital to further improve the durability and scalability of the rationally designed catalytic systems for the conversion plastic wastes to meet the demands for the future large-scale industrial applications.

Generally, sustainable energy-driven photo-/electro-chemical catalytic technology provides an efficient route for the transformation of plastic wastes to produce valued chemicals and fuels under mild conditions. Moreover, the transformation process of plastic waste can also offer an alternative feedstock. By rational regulation of catalyst and catalytic system, the photo-/electrochemical technology will be an appealing energy efficient, environmentally benign, and economically feasible method for the treatment of plastic wastes. These strategies will significantly reduce the amount of plastic waste and create an eco-friendly circular economy in the future. Implementing the sustainable photo-/electrocatalytic strategy could facilitate a low-carbon circular economy, which could alleviate energy and ecological crises in the future.

## Credit authorship contribution statement

**Jianying Wang:** Conceptualization, Investigation, Writing-original draft, Visualization, Funding acquisition. **Xin Li:** Conceptualization, Investigation, Writing-original draft, Visualization. **Ting Zhang:** Writing-review & editing. **Xufang Qian:** Writing-review & editing. **Tianfu Wang:** Writing-review & editing, Funding acquisition. **Yixin Zhao:** Conceptualization, Writing-review & editing, Supervision, Funding acquisition.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

This is the review paper. The data is taken for other works with permissions.

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